

MODELLING OF LIQUID-VAPOUR EQUILIBRIA IN THE H₂O-CO₂-H₂S-NaCl SYSTEMDUBESSY, J.¹, TARANTOLA, A.²¹UMR G2R and CREGU, Université Henri Poincaré, BP-239-54506, Vandoeuvre-lès-Nancy Cedex, France.²Mineralogische-Petrographisches, Institut der Universität, Bernouillistrasse, 32, CH-4056, BASEL, Switzerland.

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Knowledge of liquid-vapour equilibrium is essential for proper interpretation of the role of fluids in many geological environments such as sedimentary basins, hydrothermal deposits and metamorphism. Gases, combined with the salting out effect, are known since a long to increase the domain of immiscibility in the P-T plane. In addition, the interpretation of bulk homogenisation temperature of fluid inclusions of the H₂O-gas-salt systems is till now poorly interpreted due to the lack of relevant thermodynamic models of such complex systems since equations of states of complex salt-bearing fluid mixtures are still in their infancy. Therefore, the aim of this work is to present an unsymmetrical model based on the Henry law for gas concentrations lower than a few mole % and below the critical temperature of pure water.

The equations describing the phase equilibria are the following:

$$f_{H_2O}^{vap} = f_{H_2O}^{aq} ; f_{gas}^{vap} = f_{gas}^{aq}$$

The fugacity of the different components in the gas-rich phase is described by a modified Peng-Robinson equation of state with the reasonable assumption of zero concentration of salt in this phase. As the Henry's law is by definition a limiting law, the extension of this law to pressure significantly above the saturation pressure of the pure solvent requires the Krichevsky and Kasarnovsky equation:

$$\ln \left(\frac{f_{gas}^{aq}}{y_{gas}^{aq}} \right) = \ln K_{gas,aq}^{Psat} + \frac{\int_{P_{sat}}^P \overline{v_{gas}^{\infty}} dP}{RT} = \ln K_{gas,aq}^{Psat} + \frac{\overline{v_{gas}^{\infty}} \cdot (P - P_{sat})}{RT}$$

where $\ln K_{gas,aq}^{Psat}$ is the Henry constant and $\overline{v_{gas}^{\infty}}$ is the molar volume at infinite dilution of the considered gas.

The water fugacity in the liquid phase is calculated from the water fugacity in the unary H₂O system corrected by the gas concentration (x_{gas}^{aq}) and the Poynting correction equation due to the effect of pressure:

$$f_{H_2O}^{aq} = f_{pureH_2O}^{aq} * \left\{ (1 - x_{gas}^{aq}) * \exp \left[\int_{P_{sat}}^P \frac{\overline{V_{H_2O}^{liq}}}{RT} dP \right] \right\} = \{ P_{sat} \cdot \varphi_{pureH_2O}^{sat} \} * \left\{ (1 - x_{gas}^{aq}) * \exp \left[\int_{P_{sat}}^P \frac{\overline{V_{H_2O}^{liq}}}{RT} dP \right] \right\}$$

where $\varphi_{pureH_2O}^{sat}$ is the fugacity coefficient of water along the saturation line of pure water, calculated by the equation of state for the vapour phase, and $\overline{V_{H_2O}^{liq}}$ is the molar volume of pure water.

At this step, the model does not take into account the effect of the gas concentration on the activity coefficients of water and gas itself in the liquid aqueous phase. Therefore, we considered a Margules development of the excess energy:

$$\frac{G^E}{RT} = x_1 x_2 (A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots) \quad \text{and} \quad \ln \gamma_i = \frac{\partial(nG^E/RT)}{\partial n_i}$$

At the first order, it results the following equations for coefficient activity of gas and water in the liquid aqueous phase:

$$RT \ln \gamma_{gas}^{aq} = (A - 3B) * (x_{H_2O}^{aq})^2 + 4B * (x_{H_2O}^{aq})^3 - A - B$$

$$RT \ln \gamma_{H_2O}^{aq} = (A + 3B) * (x_{gas}^{aq})^2 - 4B * (x_{gas}^{aq})^3$$

where $x_{H_2O}^{aq}$ and x_{gas}^{aq} are respectively the water and gas concentration in the aqueous phase

The A and B parameters are fitted over the experimental data.

The salt was considered to produce two effects: i) a modification of the activity of water in the liquid solution and ii) a salting out effect. The first effect is quantified using the Pitzer model. For the salting out effect, an extension of the Setchenow equation was considered:

$$K_{gas, aq, m_{NaCl}}^{Psat} = K_{gas, aq}^{Psat} \cdot 10^{m_{NaCl} \cdot \beta(T)}$$

where m_{NaCl} is the salt concentration (molality scale) in the aqueous phase and $\beta(T)$ is a function fitted over the experimental data.

This model allows the calculation of the projection of the isopleths of the liquid aqueous-rich phase in the P-T plane below 300° C and 1 kbar. It is worth noting that the model is consistent with the composition of the vapour phase although it was not fitted from the few available experimental data. The model can be used for a good estimation of the pressure at the homogenisation temperature of aqueous-rich fluid inclusions. It is also a good tool for the estimation of the gas concentration in the aqueous phase at fixed P, T, m_{NaCl} in synthetic fluid inclusions formed in the aqueous phase coexisting with a vapour phase.

